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# On-site mercury analysis of soil at hazardous waste sites by immunoassay and ASV

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**Abstract**

Two field methods for Hg, immunoassay and anodic stripping voltammetry (ASV), that can provide onsite results for quick decisions at hazardous waste sites were evaluated. Each method was applied to samples from two Superfund sites that contain high levels of Hg; Sulphur Bank Mercury Mine site, Clear Lake, California, and Carson River Mercury site, Nevada. Two laboratory methods were used for comparison purposes; cold vapor atomic fluorescence spectrometry (CVAFS) and inductively coupled plasma-mass spectrometry (ICP-MS). The immunoassay was found to be accurate for high and low Hg concentrations compared to the 5 and 15 $\mu$g/g soil sample standards provided with it. Despite poor agreement between immunoassay and confirmatory analysis results at concentrations near the comparison standards, the immunoassay could be used as an effective screening method provided care is taken in identifying an operational screening level. The ASV method had an analytical range of 1–50 $\mu$g/g, with a CV of 15%. ASV results were comparable to CVAFS (CV = 15%) and more precise than ICP-MS (CV = 20%). The lower limit of quantitative results was 3 $\mu$g/g for field samples, and is attributed to uncertainty associated with sampling. 

## 1. Introduction

The characterization and cleanup of a hazardous waste site involves acquiring and analyzing numerous samples. The US Environmental Protection Agency (USEPA) is interested in evaluating analytical technologies that provide fast, inexpensive on-site results that can facilitate remediation activities by minimizing delays and reducing costs. Cost effective field methods can increase the information concerning hazardous pollutants with respect to location, source, and concentration and reduce the uncertainty in assessment of environmental health and human exposure. Few field methods for determining Hg concentrations in soil have been reported. A headspace analysis method using a Au-film Hg vapor detector has been described by Kriger and Turner (1995). This method had a detection limit of 2 $\mu$g/g and an upper linear range of 60 $\mu$g/g when applied to field soil samples. X-ray fluorescence spectroscopy (XRF) has also been used, but has a relatively high detection limit (50–60 $\mu$g/g) com-

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pared to site action levels (Hewitt, 1995; Goldstein et al., 1996). Szurdoki et al. (1995a, b, 1997) have reported on a chelate-linked assay for detection of mercuric ions down to 1 ng/g in water. However, this method has yet to be applied to field samples and or sample extracts.

The authors report on the results for two Hg field analysis methods applied to samples from US Environmental Protection Agency (USEPA) superfund sites; Sulphur Bank Mercury site, Clear Lake, CA, and Carson River Mercury site, NV. One method is a fully portable immunoassay with semi-quantitative results and the other method is a portable anodic stripping voltammetry (ASV) procedure that has quantitative results. Previous field studies with the test-tube format of the immunoassay involved approximately 14 field samples (USDOE 1994; Waters et al., 1997). The conclusion of these previous studies was that the immunoassay showed promise as a field screening technique, though several sample replicates suggested a lack of reproducibility. Two laboratory techniques, inductively coupled plasma-mass spectrometry (ICP-MS) and cold vapor atomic fluorescence spectrophotometry (CVAFS), were used as comparison methods. CVAFS is a long-established benchmark method for Hg analysis (Dumarey et al., 1985; Bloom and Fitzgerald, 1988) while ICP-MS is less commonly used (Brown et al., 1995).

## 2. Methods

Field and laboratory methods for determination of total Hg were compared primarily through analysis of sample splits generated in the following manner. Approximately 70 g of soil was gently crushed to separate particles, passed through a 2-mm sieve, and mixed with a spatula. The sample was then split into three approximately 20-g subsamples using a riffle splitter. The few high moisture samples (less than 5%) were well mixed and subsampled with a spatula. The number of field samples available in this study was 142, including 55 samples collected at each field site and 32 archived samples from a previous USEPA study of the Carson River Mercury site. Two performance evaluation (PE) standards, NIST SRM 2710 ($32.6 \pm 1.8$ $\mu$g Hg/g) and a 1:1 dilution of NIST SRM 2711 with clean sand (3.12 $\mu$g Hg/g), were run periodically by each method. Additional within-method sample splits were independently extracted and run to assess within-method variability. The within-method splits are referred to as duplicates to avoid confusion with the between-method sample split terminology.

Immunoassay and ASV analysis were performed on site for field samples and in a laboratory for the archived samples. ICP-MS analysis took place at the Lockheed Martin Laboratory, Las Vegas, NV. CVAFS was performed at the University of Nevada, Reno.

### 2.1. Field sites

Background levels of Hg in soils are typically less than 0.3 $\mu$g/g (Andersson, 1979; Lindqvist et al., 1991; Nilsson et al., 1989). At the Sulfur Bank site over 1.2 million tons of Hg-contaminated overburden and mine tailings were distributed over a 50 ha surface area due to mining operations from 1865 to 1957. Previous investigations reported concentrations in soil, overburden, and mine tailings at the site from 1 to 1000 $\mu$g/g. The area is actively precipitating sulfide deposits and HgS (cinnabar) is the predominant species at this site (USEPA, 1994). Samples were taken along four transects within the area of tailings and overburden. An additional set of samples were taken along a fifth transect 1 km east of the site to ensure low concentration samples were included in the study. Background levels of Hg in the region are 1–2 $\mu$g/g (USEPA, 1994).

The Carson River site lies within the Carson River and Washoe Lake drainage basins of Nevada. It is contaminated with as much as 200,000 flasks ($6.75 \times 10^6$ kg) of elemental Hg imported into the region for Au and Ag mining operations in the late 1800's (Bailey and Phoenix, 1944). The Hg has since been distributed over a 100 $km^2$ area by fluvial and eolian processes with much of the Hg concentrated along the Carson River drainage (Gustin et al., 1994). Mercury species include the elemental form and water soluble species; especially $HgCl_2$, and HgS. Mercury levels range from $<0.3$ to 2500 $\mu$g/g (of up to 50% elemental Hg) (Lechler et al., 1995). Samples were obtained at 13 locations, with three locations representative of regional background outside the area of contamination.

The USEPA level of action for Hg in residential soils is 23 $\mu$g/g, assuming that the Hg is present as $HgCl_2$ (USEPA, 1996). However, the remediation target levels at the Sulfur Bank and Carson River sites are 80 $\mu$g/g (Hogan and Smucker, 1994; USEPA, 1994) due to higher fractions of less soluble Hg species. For the quantitative tests in this study, the lower quantitative target level was 1 $\mu$g/g Hg.

### 2.2. ICP-MS method

The ICP-MS protocol is based on CLP-M Version 9 of EPA Method 6020 (Office of Solid Waste and Emergency Response, USEPA, Washington, DC). Although Hg is not a listed analyte, previous use of this method on soil samples for Hg has been demonstrated (Dobb et al., 1994a, b). The extraction conditions for the method are summarized in Table 1. Instrument characteristics for ICP-MS are given in

Table 1
Summary of soil extraction features for each method

| Parameter | Analytical method[a] | | | |
|---|---|---|---|---|
| | IA | ASV | ICP-MS | CVAFS |
| Sample size (gr) | 5 | 1 | 2 | 1 |
| Digestate ($HCl:HNO_3:H_2O$, v:v:v) | 2:1:1 | 1:6:17 | 1:6:17 | 3:7[b] |
| Digestate volume (ml) | 4 | 5 | 24 | 10 |
| Temperature (°C) | Ambient | 95 | [c] | 190 |
| Time (min) | 10 | 30 | 35 | Overnight |

[a] IA: immunoassay, ASV: anodic stripping voltammetry, ICP-MS: inductively coupled plasma-mass spectrometry, CVAFS: cold vapor atomic fluorescence spectroscopy.
[b] $H_2SO4:HNO_3$, v:v.
[c] MDS-2000 microwave (CEM Corp., Matthews, NC) at full power.

Table 2. Though tungsten oxide could interfere with the Hg isotopes that were monitored, this possibility was minimized by preliminary tests of target matrices for W and by performing the analysis at temperatures above the stability range for the oxide.

Activities taken to optimize sensitivity for the ICP-MS technique and verify performance include: tuning to maximize counts was performed on Bi rather than Co, using selected ion monitoring in place of the scan mode, and using calibration blanks to indicate the presence of Hg. The analysis of interference check solutions was not performed due to the absence of interference in this part of the mass spectrum (M/Z 6–150 amu). Internal standards were added by on-line addition to the uptake tube. This method guaranteed their presence, allowed the rate of addition to be optimized using presample analysis blank solutions, and eliminated pipetting and mixing uncertainties. Calibration levels were 0, 1, 10, and 25 μg/l. Between-sample rinse solutions containing 2.5 mg/l $AuCl_3$ and 6% $HNO_3$ were used to prevent carryover. The $Au^{3+}$ purges the ICP-MS of Hg, effectively removing residual surface-bound Hg that could otherwise act as a source for carryover signal between samples. Quality control protocols described in Ecker et al. (1994) were followed to ensure instrument stability and minimal carryover.

Data reduction utilized area counts-per-second (acps) for the analyte of interest and an internal standard. The acps of isotopes $^{200}Hg$ and $^{202}Hg$, representing 52.93% of the natural abundance of Hg, are summed to generate a raw intensity. During the same scan, the signal intensity (in acps) is determined for the internal standard, $^{209}Bi$. The ratio of analyte intensity to internal standard intensity is the raw intensity ratio. The same procedure is used after running a blank sample to determine a blank intensity ratio. A net intensity ratio is calculated as the raw intensity ratio

Table 2
Instrumental characteristics for ICP-MS analysis

| Parameter | Setting |
|---|---|
| Instrument | VG PlasmaQuad PO2+ (VG Elemental, Winsford, Cheshire, UK) ICP-MS |
| Rf power | 1.2 kW |
| Reflected power | < 5 W |
| Nebulizer gas flow | 0.69 l/min Ar |
| Auxiliary gas flow | 0.20 l/min Ar |
| Coolant gas flow | 13 l/min Ar |
| Nebulizer | Hildebrand grid |
| Spray Chamber | Chilled Scott Spray Chamber @ 4°C |
| Sampling height (above load coil) | 4.5 mm |
| Solution uptake rate | 1.2 ml/min |
| Rinse solution | 2.5 mg/l $Au^{3+}$ in 6% v/v $HNO_3$ |
| Sampler, skimmer cones | Nickel (1 mm orifice, 0.7 mm orifice) |
| Masses (peak dwell time, μs) | $^{159}Tb$ (2560), $^{200}Hg$ (40960), $^{202}Hg$ (40960), $^{203}Tl$ (2560), $^{205}Tl$ (2560), $^{209}Bi$ (2560) |
| Integration method | Constant area — 0.9 amu |
| Data collection parameters | Pulse collector, 10 sweeps, 5 points/peak, 5 DAC-steps/point |

minus the blank intensity ratio. Net intensity ratios are plotted vs standard concentrations and calibration curves are generated from linear least square analysis with a forced zero-intercept.

### 2.3. CVAFS method

Table 1 summarizes the sample extraction procedure for CVAFS. Digestate aliquots were added to nanopure water and Hg was purged from solution using ultra-high purity $N_2$ after addition of $SnCl_2$. Mercury was collected on Au-coated quartz sand traps, which were analyzed by dual amalgamation and CVAFS (Bloom and Fitzgerald, 1988; Dumarey et al., 1985). This technique was modified from that pioneered by Bloom and Crecelius (1983) to more closely replicate the digestion procedure associated with the immunoassay technique by omission of a BrCl oxidation step.

### 2.4. ASV method

The ASV method developed for this study has also been called constant-current stripping analysis or chronopotentiometric stripping analysis (Estela et al., 1995). Instrumentation consisted of a PSU20 potentiometric stripping unit (Radiometer Analytical Group, Westlake, OH) equipped with a glassy carbon working electrode, Ag–AgCl reference electrode, and Pt counter electrode. Prior to sample analysis, the glassy carbon electrode is plated with Au to complete the working electrode. The ASV sample extract (see Table 1 for extraction conditions) is treated with tribasic sodium phosphate to precipitate Fe, an interference, before addition to the supporting electrolyte. The working electrode is rotated at 350 rpm for 10 s at +25 mV. Stirring is then stopped and, after 30 s to achieve quiescence, the potential is scanned from 0 to +700 mV at a stripping current of 1 $\mu$A to obtain a background trace. A sample scan was obtained by repeating the procedure with a 70 s plating time. Quantitation is based on a 2-point standard addition procedure with minimum acceptable correlation coefficients of 0.995. Sample curves were inspected to confirm that the Hg peak was narrow, symmetrical, and continuous. The method has a working range of 40–2000 $\mu$g/l, which corresponds to Hg soil concentrations in a range from 1 to 50 $\mu$g/g.

The instrumental ASV detection limit, $L_D$, was estimated as $\bar{x} + [2 \times t_{0.05,\,1,\,n-1} \times \hat{s}] = 4 + [2 \times t_{0.05,\,1,\,24} \times 7.3] = 29\ \mu$g/l (Currie, 1995) based on blank samples. A 1 $\mu$g/g soil sample corresponds to approximately 40 $\mu$g/l solution concentration; the detection limit was below the desired lower quantitative limit for this application. In addition, a high level, 1000 $\mu$g/ml, aqueous quality assurance (QA) standard was periodically run by ASV as a QA check.

### 2.5. Immunoassay method

The immunoassay in this study was the BiMelyze® Hg assay tube kit for solid matrices (BioNebraska, Lincoln, NE). The method is based on the binding characteristics of Hg-specific monoclonal antibodies (Wylie et al., 1991, 1992) and involves four incubation steps that take place after sample extraction following the conditions shown in Table 1. The extract is neutralized with 7 ml of kit-provided sample buffer and filtered prior to analysis. Buffered extracts were assayed following the kit insert protocol, with absorbance measured at 405 nm using a BiMelyze® Differential photometer (BioNebraska, Lincoln, NE). Mercury concentration is positively correlated to absorbance and unknown samples are classified with respect to results from kit-supplied standards at 5 and 15 $\mu$g/g. Each kit also contains a Hg free null standard (blank) and is capable of analyzing 16 samples.

### 2.6. Design

The principal comparison between methods is made by comparing results from sample splits. Each method has its own unique extraction procedure, these are summarized in Table 1. The extraction procedure is considered just as much a part of the method as the detection procedure. It is noted that only a fraction of the test samples were run by CVAFS, so these results can be viewed as either a QA/QC or a confirmatory result.

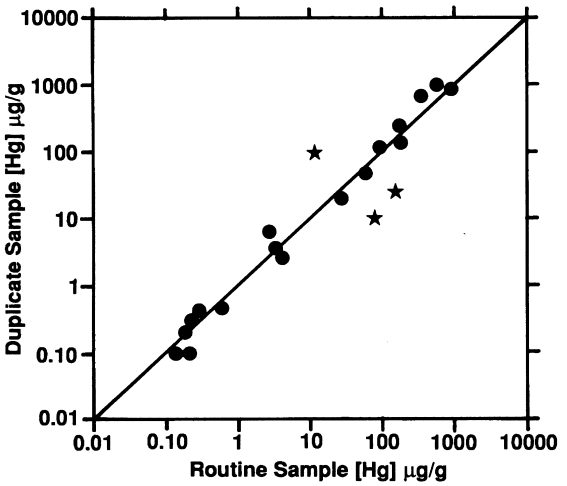


Fig. 1. Duplicate vs routine inductively coupled plasma-mass spectrometry (ICP-MS) results for field samples. Statistical outliers denoted as ★. Diagonal line represents 1:1 agreement between duplicate measurements, (——).

## 3. Results

ICP-MS accuracy was assessed from analysis of the high- and low-level PE samples. The mean ICP-MS result for the low-level PE sample was $2.54 \pm 0.05\ \mu g/g\ (n = 7)$, or 81% of the expected value. The mean ICP-MS value for the high-level PE sample was $33.0 \pm 4.7\ \mu g/g\ (n = 7)$, or 101.2% of the expected value and consistent with the certified concentration. Variability of ICP-MS was estimated from 20 sample duplicates which were independently extracted. Good agreement for all but three samples is apparent in Fig. 1. However, the variance for all 20 duplicate samples was significantly different from the variance for the 17 consistent samples ($F$ test at $\alpha = 0.05$). A robust analysis of the distribution of paired differences (Singh, 1993) suggested that the three outlying samples were not representative of the population of the remaining samples. The coefficient of variation (CV) for ICP-MS based on 85% of the data represented by the 17 duplicate pairs was 20%.

Analysis of the low level PE samples by CVAFS gave $3.23 \pm 0.80\ (n = 5)$; within experimental error of the expected value. The average CV for duplicate samples analyzed by CVAFS was 15% ($n = 19$).

CVAFS results for field samples are compared to ICP-MS results in Fig. 2. The least square fit equation is log([Hg] by CVAFS) = [0.90 × log([Hg] by ICP-MS)]−0.16, (the concordance correlation coefficient (Lin, 1989) for the log-transformed values is $R_C = 0.88$). The least square fit line suggests significant bias towards higher ICP-MS Hg concentrations above 100 μg/g, but little or no bias at low concentrations.

ASV results for the low- and high-level PE samples were $3.79 \pm 1.13\ (n = 8)$ and $30.4 \pm 3.7\ (n = 19)\ \mu g/g$, respectively. Results from ASV analysis of 41 duplicate samples (Fig. 3) show good relative precision down to 3 μg/g. The 1000 μg/ml QA sample results gave a statistically significant bias of +3% ($p = 0.029, n = 11$). However, for field sample analysis, this bias was too small to adversely impact the results relative to other sources of variability. The CV of 11 high level performance samples prepared as a solution was 5% using ASV. This variability estimate can be contrasted with uncertainty estimates based on the overall ASV method. Results for 29 samples where both routine and duplicate ASV analysis were above 3 μg/g (Fig. 1) were internally consistent with the exception of 1 outlier. The CV for ASV from the 28 consistent duplicate pairs is 13%, and $R_C$ for the log-transformed values is 0.99. The CV from the QA samples include variability over several weeks of analysis while the CV from duplicate pairs represents variability within one or between two days.

ASV results for field samples are compared to ICP-MS results in Fig. 4. Samples below approximately 3 μg/g are randomly scattered across the low concentration range. Most of the 100 samples above the 3 μg/g level are clustered about the 1:1 line, though 5% have results that differ by a factor of 10. For the samples above 3 μg/g, the concordance correlation coefficient comparing log-transformed results is 0.94. Variability between methods estimated from the 100 samples with concentrations greater than 3 μg/g by

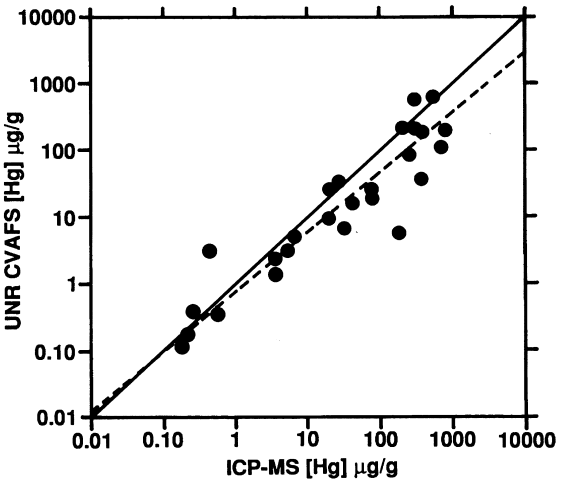


Fig. 2. Comparison of cold vapor atomic fluorescent spectroscopy (CVAFS) results from the University of Nevada, Reno vs ICP-MS results for 26 field samples. The least square line is: log([Hg] by CVAFS) = [0.90 × log([Hg] by ICP-MS)]−0.06, (- - - - -). Diagonal line represents 1:1 agreement between method measurements, (——).

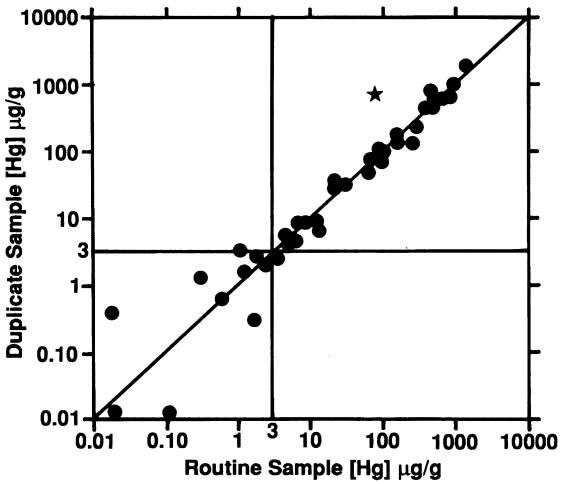


Fig. 3. Duplicate vs routine anodic stripping voltammetry (ASV) results for field samples. Statistical outliers denoted as ★. Diagonal line represents 1:1 agreement between duplicate measurements, (——).

both methods was 21.6%. An independent estimate for this value based on duplicate ICP-MS and duplicate ASV results gave a CV of 23.8%.

CVAFS Hg concentrations were somewhat lower than the ASV results. The least square fit for the log-transformed data was log([Hg] by CVAFS) = [0.847 × log([Hg] by ASV)] + 0.015 ($R_C$ = 0.87, n = 26). This relationship is in agreement with expectations from modification of the CVAFS extraction protocol to mimic the immunoassay, which might have resulted in a lower extraction efficiency.

The Hg immunoassay is a semi-quantitative method, and cannot be evaluated with quantitative estimates for parameters such as accuracy and precision. Precision was evaluated with respect to consistency for duplicate sample analysis. Of 34 samples run in duplicate, 26 (76%) gave consistent results. However, only 56% of the duplicate immunoassay sample results were both consistent with each other and in agreement with ICP-MS results. For the duplicate immunoassay samples it is interesting to note that 8 of 9 samples with ICP-MS Hg concentrations less than 1 μg/g and 9 of 9 samples with ICP-MS Hg concentrations over 100 μg/g were correctly classified. However, 14 of 16 samples with ICP-MS Hg concentrations between 1 and 100 μg/g were incorrectly classified by the immunoassay.

Immunoassay and ICP-MS field sample results are compared with a contingency matrix (Table 3). This matrix shows that most samples in the range between the 5 and 15 μg/g internal standards are misclassified by the immunoassay technique compared to ICP-MS. There is a slight improvement in accuracy to 73% when the samples are classified by only the 15 μg/g standard.

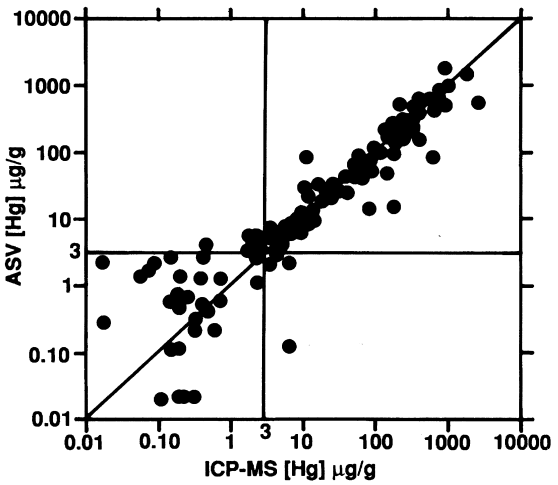


Fig. 4. ASV vs ICP-MS results for field samples. Diagonal line represents 1:1 agreement between method measurements (——).

Field sample results for immunoassay are compared to ICP-MS levels in Fig. 5 for the Sulphur Bank, field Carson River, and archived Carson River samples. In Fig. 5(a) immunoassay classification is biased low compared to ICP-MS. Fig. 5(b) shows good results for the 5–15 μg/g interval, but numerous samples are biased high with regards to ICP-MS. Fig. 5(c) shows all 5–15 μg/g samples as either misclassified above or below the expected concentration range. An alternate description is to say all 5–15 μg/g samples fall into either the false positive or false negative category. The results are consistent with a large variability associated with immunoassay and/or ICP-MS. However, the variability described above for ICP-MS analysis is less than the variability seen in these classification plots. A parallel analysis comparing immunoassay classification to ASV results (results not shown) produced virtually identical results.

The inconsistency in immunoassay classification with respect to ICP-MS and ASV could be related to many factors. Since each method analyzed a separate subsample, subsampling uncertainty affects the reported Hg level from each method. However, one would not expect identical effects from either method. Rank correlation coefficients were calculated for each pairing of methods using all field sample results (Table 4). Immunoassay results were set to 5, 10, or 15 instead of < 5, 5–15, and > 15 for these calculations. The results show each pair of quantitative methods correlated from 0.91 to 0.96 while all comparisons to the immunoassay ranged from 0.63 to 0.76. The semiquantitative nature of the immunoassay results do have an effect on the correlation coefficients. From the authors' experience, the correlation coefficients with one semi-quantitative method are expected to be about 0.1 unit lower than had quantitative values been available. However, this adjustment still leaves the immunoassay values at least 0.1 below the coefficients for the other method comparisons. This suggests the uncertainty in the immunoassay comparisons is largely inherent to the assay.

Kido et al. (1999) found that an ELISA-format chelating sensor method for Hg overestimated the Hg concentration in Carson River water samples when compared with CVAFS. They attributed this to the presence of other metals in solution. The BiMelyze® immunoassay yielded a higher percentage of false positive readings (64%) for samples from the Carson River site than for the Sulphur Bank site (27%). This could be attributed to the additional metals that would be present in the Carson River samples. The Carson River samples contain Au, Ag, Zn, Pb, and As (cf. Hogan and Smucker, 1994) as a result of the area being a Au and Ag mining district, whereas the Sulfur Bank samples contain primarily Hg. Also, the Hg

Table 3
Classification matrix comparing immunoassay results to ICP-MS results[a]

| | | Immunoassay | | | *n* Total | Correct (%) |
|---|---|---|---|---|---|---|
| | | < 5 | 5–15 | > 15 | | |
| ICP-MS | < 5 | 33 | 4 | 12 | 49 | 67 |
| | 5–15 | 5 | 5 | 12 | 22 | 23 |
| | > 15 | 4 | 11 | 56 | 71 | 79 |
| | *n* Total | 42 | 20 | 80 | 142 | |
| | Correct (%) | 79 | 25 | 70 | | 66 |

[a] *n* is the total number of samples within either a row or column. The correct (%) value is the percent of each *n* row or column samples which were correctly classified.

extraction for the immunoassay consisted of a 50% acid digestion at ambient temperature, a much lower relative acid volume and temperature than extractions for the other methods. Depending on the amount and species of Hg in the sample, this might also be related to inconsistent results.

The immunoassay kit standards were run with each batch of samples to allow adjustment for the effect of slightly different conditions (e.g., timing, temperature) for each analysis. A plot of absorbance response for the 5 and 15 μg/g kit standards shows high variability between the two standards (Fig. 6). One would expect both standards to shift in a similar manner if factors such as timing or temperature were changing between kit runs. These results suggest a source of within-run variability for the immunoassay in the region of the standards.

## 4. Conclusions

The ASV method was demonstrated to be an excellent quantitative field method for Hg down to 3 μg/g in soil, a level believed to be associated with this study's sampling uncertainty. The estimated CV of 13% includes sampling, extraction, and analysis uncer-

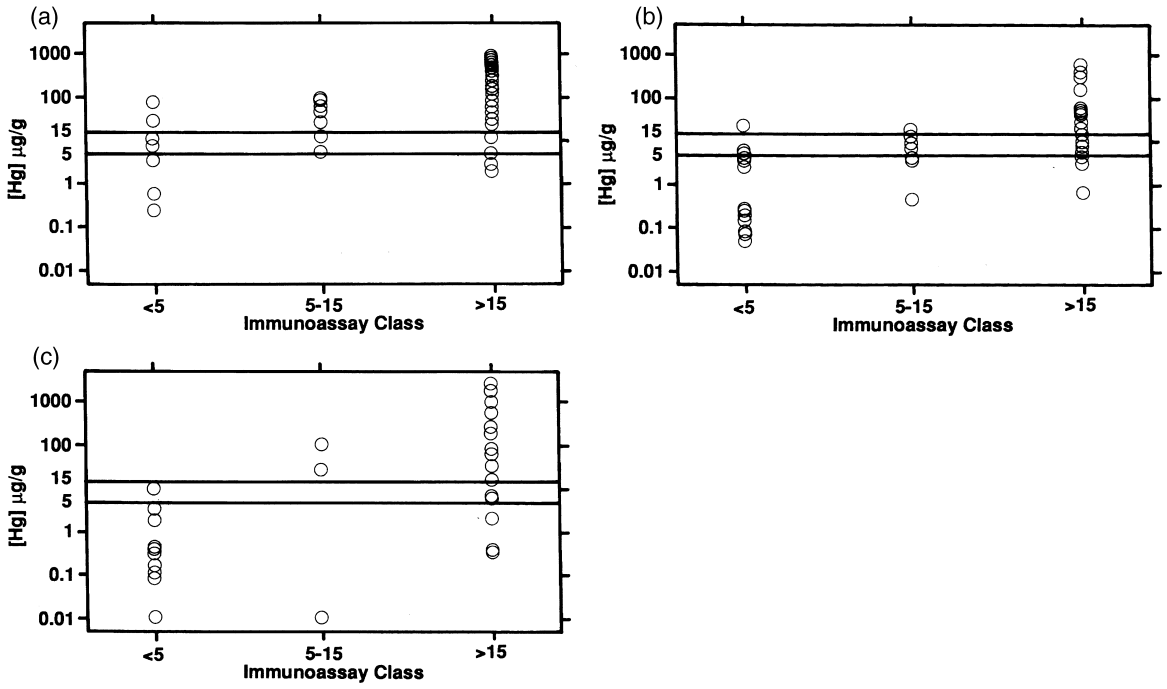


Fig. 5. ICP-MS results displayed by immunoassay class for (a) Sulfur Bank samples, (b) field Carson River samples, and (c) archived Carson River samples.

Table 4
Rank correlation coefficients for field sample result comparison between methods

| Method comparison | $R_R$ [a] | Sample size ($n$) |
|---|---|---|
| ICP-MS vs ASV | 0.96 | 141 |
| ICP-MS vs IA | 0.64 | 142 |
| ICP-MS vs CVAFS | 0.90 | 26 |
| ASV vs IA | 0.63 | 141 |
| ASV vs CVAFS | 0.91 | 26 |
| IA vs CVAFS | 0.76 | 26 |

[a] $R_R$: Rank correlation coefficient.

tainty. The variance associated with characterizing field soil concentrations is often much larger than the variance associated with analysis of an individual aliquot of soil (Pitard, 1989). The ASV method gives on-site results acceptable for many hazardous waste site characterization, monitoring, and decision-making processes. The method was automated, yet quite flexible, allowing the analyst to adjust several criteria to optimize the response and minimize analytical variability. However, sites should be characterized on a case-by-case basis for chemical interferences prior to use. If necessary, lower analytical ranges can be easily achieved with increased plating time.

Immunoassay results were inconsistent in the 5–15 μg/g range of Hg concentration near the assay's decision level. Despite this, the immunoassay correctly classified samples with very high and very low concentrations with respect to the decision level range. The two, close-set internal standards appear related to the poor classification results. The range between the two standards is small compared to the uncertainty in the method, making it difficult to reproducibly classify samples between or near these concentration levels. Improved performance requires using one standard level or standard levels that are much farther apart than the factor of 3 used in this formulation of the method. In addition, immunoassay sample analysis used four steps involving several reagent additions from dropper bottles and washings between steps. Volume additions and carryover from wash steps have previously been identified as the most likely reason for inconsistent results in many environmental immunoassays (Gee et al., 1994), and may have contributed to the uncertainty observed in this study.

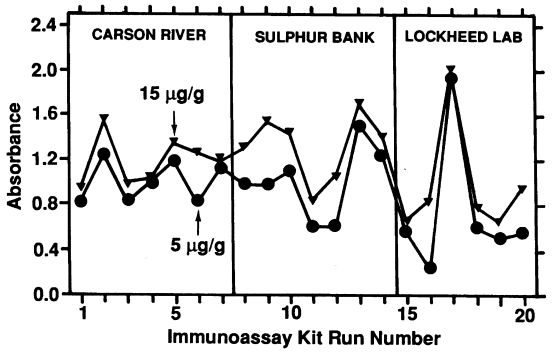


Fig. 6. Immunoassay kit standards plotted by run number by analysis locations.

In general, there was good agreement between all three quantitative methods, ASV, ICP-MS, and CVAFS. Rank correlation coefficients for intermethod comparisons were above 0.9 for each pair of methods. For most samples, the ICP-MS and CVAFS methods generated quantitative results for Hg in a laboratory setting with estimated CVs of 20 and 15%, respectively. However, despite intensive analytical control, 5–15% of the ICP-MS samples appear to have much larger errors.

In this study variability from sampling and extraction effects appear to dominate the variance below 3 μg/g for both ICP-MS and ASV field samples. The observation that the estimate of variance for ASV vs ICP-MS for field samples is similar to the sum of the independently estimated variances for ASV and ICP-MS also support this assertion. The characterization of environmental sites involves uncertainties due to sampling that can be much greater than the instrumental uncertainty component of an analytical method. Thus, efforts at achieving high precision for a laboratory method may make little contribution toward achieving field study goals if subsampling variance is high.

The acceptance of new monitoring methods requires evaluation studies based on real-world environmental samples. Characterizing Hg exposure requires estimates of concentration as well as the uncertainty associated with individual field samples rather than the small uncertainty associated with analytical instrumentation. The results of this study suggest sampling uncertainty for hazardous environmental chemicals is an area deserving further study. Information about this subject is of fundamental importance when designing future field evaluations or whenever an accepted laboratory method is applied in a field situation.

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